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NOVEL DUPLEX VAPOR-ELECTROCHEMICAL METHOD FOR SILICON SOLAR CELLS

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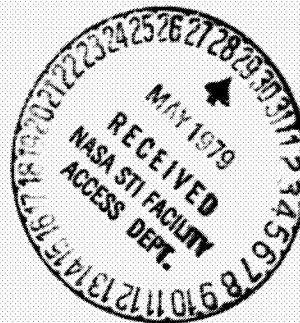Pasadena, California 91103

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CONTENTS

ILLUSTRATIONS

TABLES

PREFACE

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program aimed at the development of low cost solar arrays. The work reported here was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

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TASK 1

SiF$_4$-Na REACTION: SOLID Na FEEDING

Introduction

Optimization studies have been carried out for the SiF$_4$-Na reaction
with solid Na feed. The goals of the studies were

- The consistent production of high purity reaction products
- The gathering of relevant information needed to scale-up
  the reactor.

During the last quarter, the SiF$_4$-Na reaction has consistently yielded
reaction products whose impurity content was always below the detectability
limits of emission spectrographic analysis. Solid Na slices were fed into
the pyrex SiF$_4$-Na reactor, which was lined with a Ni foil sheath (0.01 inch
thick) to provide a mechanical support, and an inner Grafoil sheath
(0.01 inch thick) to avoid contamination of the products by contact with
Ni. The reaction products from eleven different runs were analyzed by
emission spectrography as a routine quality control measure. Calcium was
the only detectable impurity (20 to 200 ppm by weight).

Parallel to the production of pure reaction products, an effort has
been made to obtain information suitable for the scale-up of the process.
Parameters were studied in order to optimize the process. The goals were:

- To decrease percentage of unreacted Na
- To decrease percentage of produced Na$_2$SiF$_6$
- To increase overall Si production rate.

During this quarter, efforts have focused primarily on reducing the
percentage of unreacted Na remaining on the reaction products. Several
parameters that affect the amount of unreacted Na have been identified
and studied. Briefly, they are:

- Pressure of SiF$_4$
- Size of Na slice

1

- Geometry of Na slice and surface oxidation state of Na
- Rate of addition -- number of slices added per time
- Temperature of outside walls of reactor.

From previous information obtained in single batch experiments, we know that as the pressure of SiF_4 increases, the amount of unreacted Na decreases. We have therefore used SiF_4 pressures around 1 atm. the maximum safe limit for the present pyrex reactor. The effects of higher pressures have been studied in a stainless steel reactor, for single batch experiments. The reaction products obtained with SiF_4 pressures up to 10 atm were similar to that obtained at 1 atm. The effects of high SiF_4 pressures on the characteristics of the reaction products when Na is used, will be studied in a stainless steel reactor presently under construction. Each one of the other parameters mentioned above has been varied under controlled conditions in order to isolate their individual effects on the reaction, as discussed in the following sections.

Effect of Surface to Volume Ratio of Na Slices on the Extent of Reaction

The chief result of varying the ratio was that the amount of unreacted Na decreased with increasing surface to volume ratio of the Na slices. The surface to volume ratio was controlled by cutting Na slices of different thickness from a Na cylinder (6 cm. diameter). The slices were fed to a Grafoil-nickel lined 7 cm i.d. glass reactor. All other variables except external heating were maintained essentially constant for these studies. Both the upper and lower values of the amount of unreacted Na are shown in Table 1 to indicate the heterogeneity of the reaction product.

2

Table 1

EFFECT OF SURFACE TO VOLUME RATIO OF Na SLICES
ON AMOUNT OF Na UNREACTED (CYLINDRICAL SLICES)

Slice Thickness (cm)	$\frac{Surface}{Volume}$ (cm^{-1})	Weight % Na in Reaction Products
0.3	5.7	2-4, 3-5, 2-8
0.6	3.5	5-7, 3-5, 2-18, 9-20, 5-11
1.3	1.9	>20

Table 1 shows that the amount of unreacted Na decreases when the thickness of slices is reduced. A similar tendency can be observed for quadrant (pie shaped) slices, Table 2, obtained by diametral cutting of the cylindrical slices.

Table 2

EFFECT OF SURFACE TO VOLUME RATIO ON
AMOUNT OF UNREACTED Na (QUADRANT SLICES)

Slice Thickness (cm)	$\frac{Surface}{Volume}$ (cm^{-1})	Weight % Na in Reaction Products
0.6	3.9	3-9
1.3	2.9	∿5, 1-10
1.8	2.1	>20

It was concluded that for Na slices cut in air, the surface to volume ratio must be greater than 3 cm^{-1} in order to obtain less than 10 weight % unreacted Na in the mixed product NaF and Si. Further interpretation of these results will be possible when different diameter of slice to diameter of reactor ratios are studied.

3

Effect of Na Surface Oxidation on the Extent of Reaction

Good conversion was obtained with Na cut in air with no special pre-
cautions if it was immediately used in the reactor.

The presence of a surface oxide layer on Na was of concern, since it
was believed to reduce the effective surface area available for the SiF_4-Na
reaction. To study the effect of Na oxidation on the extent of reaction
with SiF_4, Na slices with different degrees of oxidation were fed to the
SiF_4-Na reactor. To obtain different oxide thicknesses, Na slices were
exposed to air for approximately 10 and 30 minutes. As a control, Na was
also sliced in an argon atmosphere and rapidly transferred, under an argon
flow, to the reactor. Table 3 shows the amount of unreacted Na in the re-
action products obtained from each type of oxidized Na.

Table 3

EFFECT OF Na SURFACE OXIDATION ON

PERCENTAGE OF UNREACTED Na (Cylindrical Slices, 0.6 cm Thick)

Oxidation State	Weight % Na In Reaction Products
Light Oxidation (Na cut in Ar)	5-11
Normal Oxidation (Na exposed to air for $\lesssim$10 min)	2.5-11,9-20,5-11
Heavy Oxidation (Na exposed to air for 20-30 min)	>20

From the information in Table 3, it was decided that the Na slices
can be cut in air without appreciably changing their reactivity if they
are loaded into the reactor within about 10 minutes. The use of an inert
atmosphere for the cut-load operation does not seem to produce any appre-
ciable improvement (i.e. decrease) in the amount of Na left unreacted.

To get a qualitative idea of the nature of the surface oxide formed
during the Na cutting and loading, Na slices of known surface area were

4

exposed to room air, and their weight change with time was recorded (Figure 1). The weight measurments started 1 minute after the Na had been initially exposed to air and continued for 35 minutes. Within this time range, the weight increase with time was linear.

The linear behavior shown in Figure 1-a, together with the microscopic observation of porosity in the oxide, indicates that the Na oxide layer formed is nonprotective.

The order of magnitude of the thickness of the oxide layer was estimated by assuming its porosity to be approximately 50%, which corresponds to an apparent density of approximately 1 gcm^{-3}. This value, the initial surface area of the Na slices (51 cm^2), and the data from Figure 1-a allowed us to estimate the thickness of the oxide layer as a function of time (Figure 1-b).

Since the oxide layer formed on the Na surface was observed to be porous and nonprotective, one would expect that the time of the exposure to air should not affect greatly the rate or extent of the SiF_4-Na reaction. The fact that it did affect the extent of this reaction was probably due to the presence of H_2O in the Na oxide layer. When Na is exposed to the laboratory air, not only Na_2O, but NaOH and Na_2CO_3 are also formed. Furthermore, the NaOH will readily absorb H_2O. In the reactor, when SiF_4 contacts the "wet" NaOH, it produces SiO_2 and NaF. The SiO_2, formed as a gel, may "plug" the porous path to the fresh Na surface and, as a consequence, the initial rate of reaction may be decreased and the residual Na increased.

Effect of External Heating on the Extent of SiF_4-Na Reaction

It was determined that the temperature maintained at the external wall of the pyrex reactor did not influence the characteristics of the reaction products. The reactor was run in two basic modes, self-sustaining, and external heating. In the self-sustaining mode, the temperature of the outside wall of the reactor was due solely to the heat generated by the reaction

5
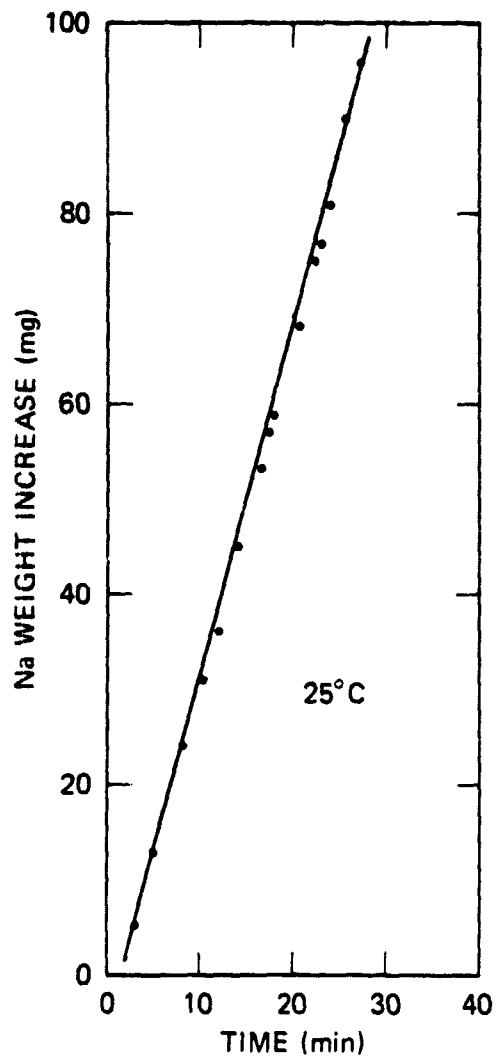
(a) **MEASURED Na WEIGHT
INCREASE WITH TIME**

51 cm² initial area.
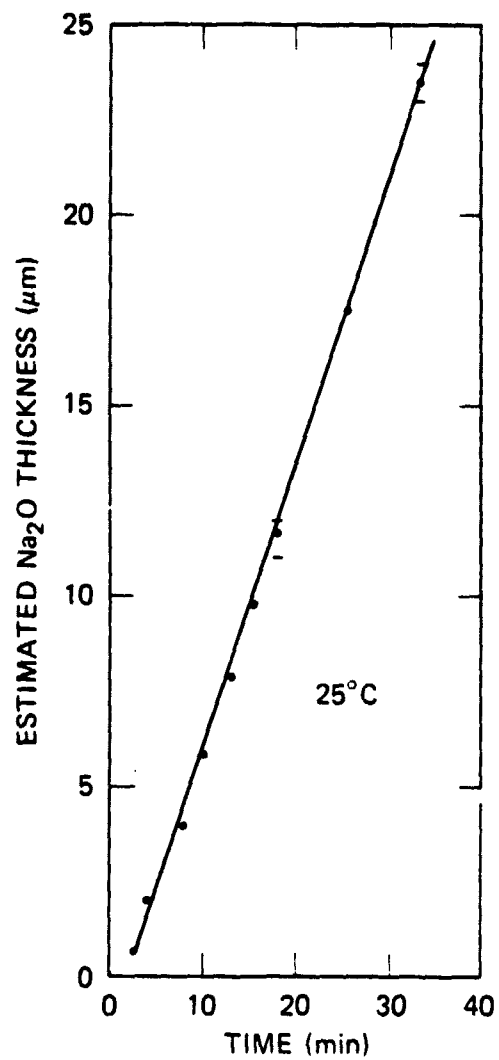
(b) **ESTIMATED Na₂O THICKNESS
INCREASE WITH TIME**

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FIGURE 1

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6

itself. At the reaction zone, the average temperature reached on the outside wall was 300°C. As the products built up with continued reactant feed, the hot region moved upwards with the reaction zone. The temperature of the already generated reaction products decayed exponentially to room temperature.

For the external heating mode, the outside walls of the reactor were maintained at approximately 400°C by heating tapes. At the reaction zone level, the temperature rose to 600°C, at which level the tapes were turned off temporarily. The upper limit of 600°C was imposed by the use of a glass reactor. It was expected that, by increasing the outside temperature, the reaction products would be kept hotter for a longer time. Thus, a more complete reaction would be attained. However, the experimental results summarized in Table 4 indicate that the external heat does not change significantly the amount of unreacted Na present in the reaction products for the limited temperature range explored with the glass reactor.

Table 4

EFFECT OF EXTERNAL HEATING ON AMOUNT OF Na UNREACTED
(Cylindrical Slices, 0.6 cm Thick)

Heating Mode	Weight % Na In Reaction Products
Self-Sustaining	3-5,5-11
External Heating	5-7,2-18,5-11,2.5-11

In Table 4, the range indicates the variation obtained with at least eight randomly selected samples taken from the reaction products of each experiment. The total weight of products in each run was usually about 0.5-1.0 kg.

Effect of Na Slice Addition Rate on the Extent of Reaction

It has been found that the content of unreacted Na in the reaction products is strongly correlated with the number of slices dropped into

7

the reactor during each Na addition. With the side arm feed[*] of the
SiF_4-Na reactor, two or more Na slices could be fed at the same time.
Figure 2 shows the correlation of amount of unreacted Na and average
number of slices added at a time, using slices of 0.6 cm thickness. The
correlation indicates that the mass of Na per addition is a key factor.
Additional studies indicate that the products obtained when several slices
are fed per addition are similar to those obtained when a single slice of
equal total volume is added. This similar behavior occurs because the Na
slices melt to form a common pool before reacting.

SiF_4-Na Reaction: High Pressure Experiments

A new SiF_4 feeding system has been built for single batch studies of
the SiF_4-Na reaction at pressures greater than 1 atm. The SiF_4 is delivered
from a high pressure (3000 psi) tank to the stainless steel reactor through
an all stainless steel line (Figure 3). Included in the line are a filter,
a constant pressure regulator, a secondary storage cylinder to condense
excess SiF_4, and necessary valves and pressure gauges.

In typical operation, the reactor was loaded with a Ni or Al_2O_3
crucible containing 5 grams of Na. The reactor was made gas tight by means
of Cu gaskets, and it was evacuated through V3 and V4. The reactor was
heated under vacuum until the Na temperature reached approximately 250°C.
At this point, vacuum valve (V3) was closed and SiF_4 was allowed into the
reactor by opening the high-flow ball-valve (V2). The use of this high-flow
valve was necessary to reach pressure equilibrium between the cylinder
source and the reactor almost instantaneously. Since the volumes of the
reactor and the cylinder were almost identical, the initial reaction pres-
sure was approximately half of the pressure in the cylinder measured at
PG 1 (Figure 3).

The first SiF_4-Na reaction, operated at 2 atm of SiF_4, yielded reaction
products similar to those obtained in runs at 1 atm. A very hard, porous
grey crust was obtained, and less Na than 5% by weight was left unreacted

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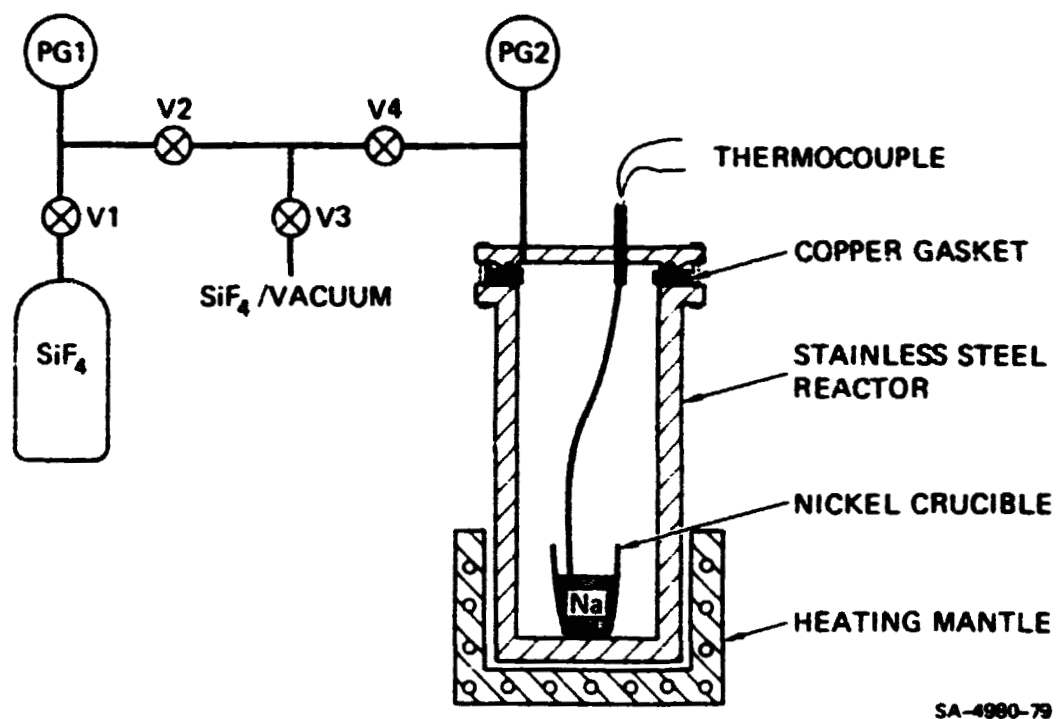[*]Quarterly Report No. 11.
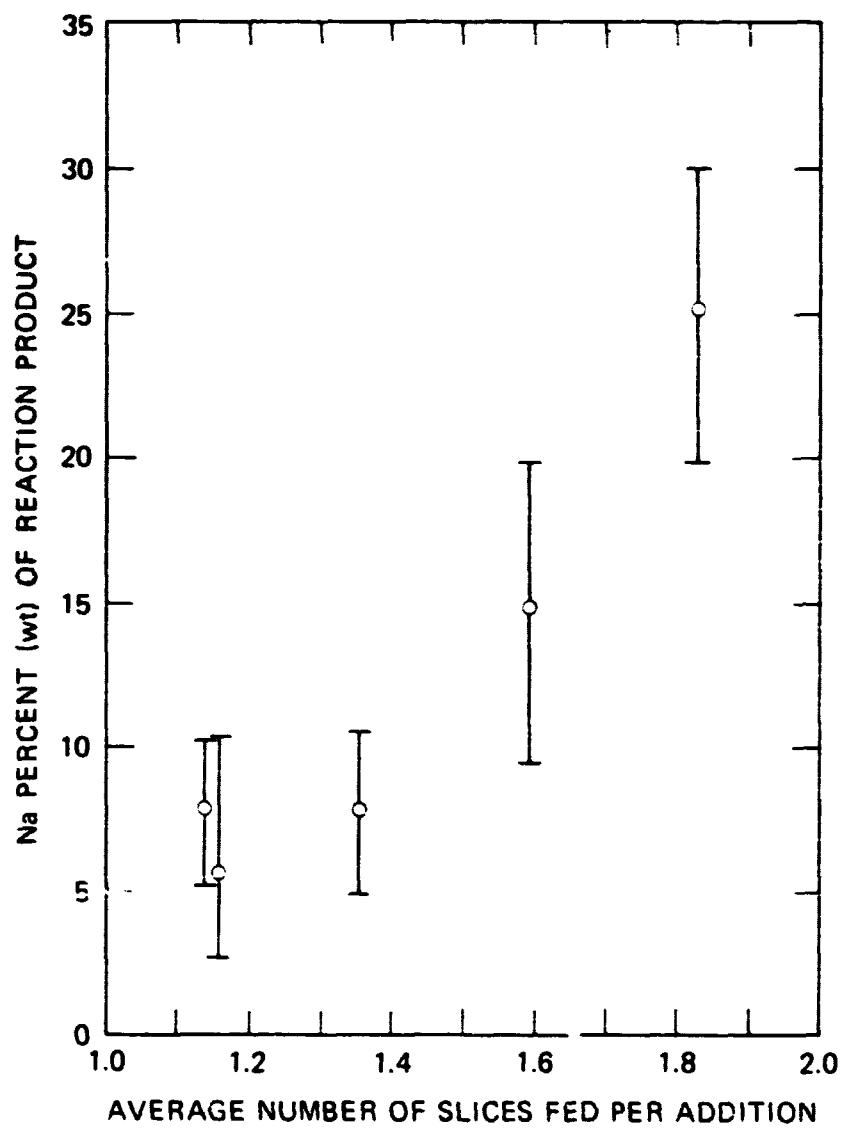
FIGURE 2   EFFECT OF THE NUMBER OF SLICES PER ADDITION
ON THE AMOUNT OF UNREACTED Na

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9

FIGURE 3   HIGH PRESSURE SiF$_4$-Na, SINGLE BATCH, REACTION SYSTEM

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(see Figure 4-a). The reaction products obtained at pressures as high as 8 atm (as shown in Figure 4-b) are also similar in morphology and composition to those obtained at 1 atm. From these single batch experiments, it seems evident that the increase in SiF_4 pressure above 1 atm does not result in a change of type of reaction products. Accordingly, pressurized reactor studies ` _ve been curtailed. The results are fortunate in that 1 atm operation is practically convenient.
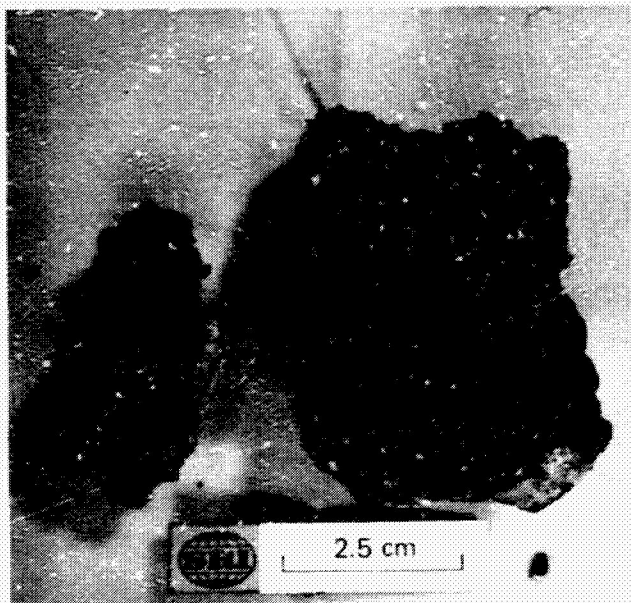
(a) $P_{SiF_4} = 2$ atm
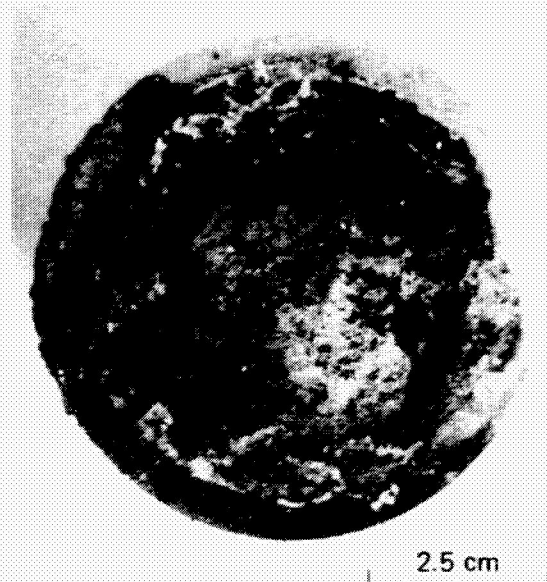
(b) $P_{SiF_4} \cong 8$ atm

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FIGURE 4   REACTION PRODUCTS FROM SiF$_4$-Na REACTION — SINGLE BATCH

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12

TASK 2

MELTING

An investigation has been made of the possible role played by NaF as a fluxing agent during the separation of silicon by melting of the reaction product (Si + NaF) mixture. In a first series of experiments, metallurgical grade silicon was mixed with NaF (Si: NaF:: 1:4 mol ratio). A thin (0.4 μm) oxide layer was thermally grown on the Si to simulate a worst case of reaction products exposed to air. The mixture of Si and NaF was loaded in a graphite boat and heated at temperatures below and above the melting points of NaF (998°C) and of Si (1410°C). It was observed that no substantial changes occurred below the melting point of NaF. Above 1000°C, molten NaF wetted the silicon grains and promoted sintering at around 1360°C (Figure 5a). The analysis by x-ray energy spectrometry (XES) of the white areas (Figure 5-b) showed the presence of Na, Si and F. XES of the dark areas showed only Si.

In order to obtain more details of the effect of the NaF on the surface silicon oxide, mixtures of NaF and silica gel were studied, using SiO_2gel in large amounts as compared with the naturally limited thin layer of SiO_2 on Si. The NaF-SiO_2 gel mixtures were heated for 10 minutes to temperatures ranging from 200° to 1500°C. The products were quenched and x-ray analyzed. No interaction was observed at temperatures below 800°C. Above 800°C, the presence of cristobalite was detected at 865°C, and tridymite at 1190°C. At 1190°C, malladrite, a form of sodium fluosilicate, was also detected. Thermodynamic estimations based on extrapolations of the value for the heat of formation of Na_2SiF_6[*] predict that, indeed, Na_2SiF_6 will be produced at temperatures above 1000°C. Furthermore, the formation of this fluorosilicate according to

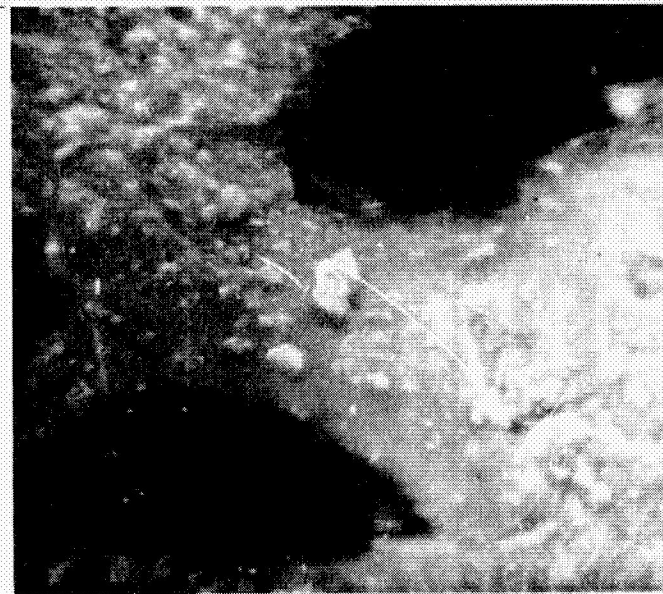$$3SiO_2(s) + 6NaF(\ell) \longrightarrow 2Na_2SiO_3(\ell) + Na_2SiF_6(s)$$
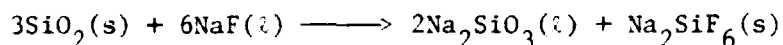
is the only possible reaction between SiO_2 and NaF with a suitable free energy of formation in the temperature range from 1000°C to 1400°C; for example, $\Delta G^\circ_{1400} = -8$ Kcal/mol.

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*Quarterly Report No. 5

13

(a) SEM PHOTOMICROGRAPH OF Si
GRAINS IN NaF AFTER 10 MIN
AT 1360°C

(b) SEM PHOTOMICROGRAPH OF NaF
PHASE NEAR Si EDGES AFTER
10 MIN AT 1360°C

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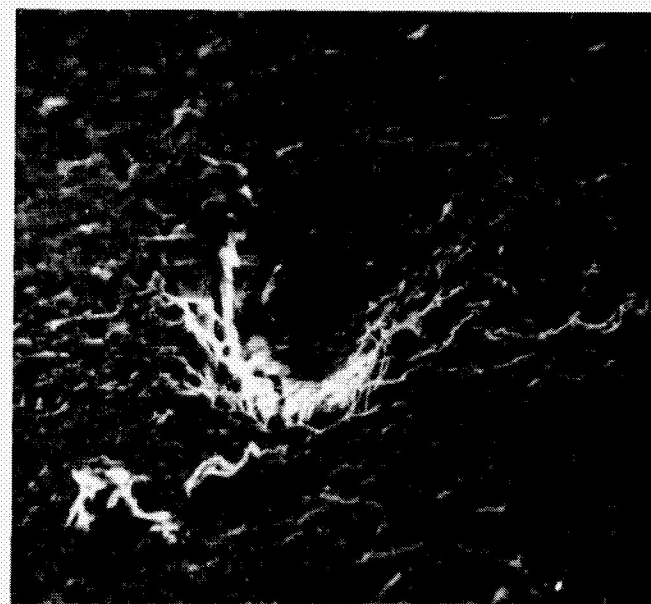
FIGURE 5

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The presence of malladrite is, therefore, consistent with both thermodynamic predictions and the information obtained by XES (Figure 5b).

A mechanism through which NaF acts as a flux agent can be postulated. Molten NaF attacks the SiO_2 structure by producing fluorosilicates soluble in liquid NaF. As a consequence, the protective SiO_2 layer on the Si is dissolved, and the now clean Si surfaces can interact directly on contact, forming bridges between Si particles (Figure 5a). At temperatures above the melting point of Si, these bridges multiply and grow until finally all the silicon grains condense into a single globule. If this process is interrupted by quenching just before total union, the interparticle voids can still be observed (Figure 6a) and white whiskers (Figure 6b) of compounds containing Si, Na and F (according to XES) can be observed within those voids. It is probable that the whiskers grew by condensation from a vapor phase in cavities remaining between incompletely fused silicon particles. The original size of the sieve fraction of crushed mg Si particles used is also shown in Figure 5a to indicate the extent of sintering and interparticle bridge formation.

400 μm

(a)   SEM PHOTOMICROGRAPH OF THE CROSS-
      SECTION OF Si GLOBULE PRODUCED BY
      HEATING Si-NaF MIXTURE AT 1510°C
      FOR 10 min.

100 μm

(b)   SEM PHOTOMICROGRAPH OF VOIDS IN
      Si GLOBULE OBTAINED BY HEATING A
      Si-NaF MIXTURE AT 1510°C FOR 10 min.

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FIGURE 6

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THERMITE

As reported previously[*] silicon can be produced by the thermite
reaction between Na_2SiF_6 and Na. In this process, slices of Na, 6 cm in
diameter and 1 cm thick, were mixed with sodium fluosilicate powder
(industrial grade) and heated to 500°C in a closed reactor to start the
reaction. The distribution of the reactants is expected to influence the
rate of heat transfer, rate of reaction propagation and completion of the
reaction. We have initiated studies to gather information on parameters
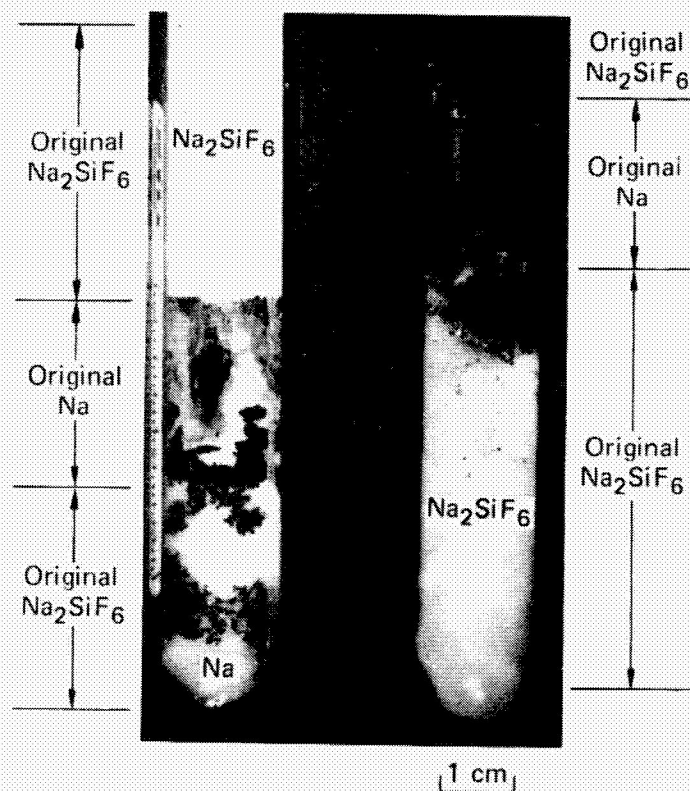which control the efficiency of the thermite reaction.

The purpose of the first set of experiments was to determine what
happens to the Na when it is heated in the presence of Na_2SiF_6 at temper-
atures below reaction "ignition" temperature (400°C). Glass tubes
(1 cm i.d. x 15 cm) were loaded with a 2-cm high column of Na_2SiF_6 powder,
on top of which was placed a Na rod (5 cm x 0.1 cm x 0.6 cm) surrounded by
Na_2SiF_6 and, topping the sandwich, another 2-cm high column of the flucrosil-
icate powder. The glass tube was evacuated and heated to selected temper-
atures. Below the 400°C reaction "ignition" temperature, most of the
sodium remained in place even after melting (98°C). This effect is most
probably due to the surface oxide layer formed on the Na metal when cut
in air. However, some liquid Na migrated along the glass walls or broke
the oxide layer, oozed out and solidified in growths that extended for
approximately 1 to 2 mm from the original surface of the Na (Figure 7a).

In a second set of thermite mechanism experiments, at temperatures
above 500°C, the thermite reaction takes place so fast that we have not
yet been able to "freeze" a partial reaction for study. We have observed
that the Na migrates through the already formed reaction products to meet
the Na_2SiF_6, leaving behind void spaces in the shape of the original Na
segments. We have also observed that the thermite reaction takes place
in one major direction within the reactant mix. This behavior may be due

*Quarterly Report No. 11.

17

0.5 cm

(a) Na STATE AFTER HEATING TO 300°C IN Na₂SiF₆

Original Na₂SiF₆

Na₂SiF₆

Original Na

Original Na₂SiF₆

Na

Na₂SiF₆

Original Na₂SiF₆

Original Na

Original Na₂SiF₆

1 cm

(b) REACTION PRODUCTS OBTAINED WHEN Na WAS HEATED TO 500°C IN Na₂SiF₆

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FIGURE 7

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to extreme localization of reaction when the first liquid Na breaks the oxide layer at one point. The heat released by the rapid reaction may "pump" the Na towards the reaction zone, causing it to move in one direction only. For example, Figure 7b shows that the reaction propagates either upwards or downwards from an identical starting configuration of reactants.